



Date: September 30 1992



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FINAL TECHNICAL REPORT

For: US Naval Research Laboratory, Project N-00014-92-P-2000  
"Characterization of Semi-Insulating Gallium Arsenide"

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ABSTRACT:

This project was established effective October 1991, to continue through September 30 1992. Its purpose has been the electrical and optical characterization of samples from melt-grown crystals of gallium arsenide (GaAs). Almost all of the samples measured during this 12-month period were "undoped" (nominally undoped), and almost all samples came from crystals grown at NRL by the vertical zone melt (VZM) method. A series of technical reports during the year (when there were new results to report to NRL), plus quarterly reports submitted after 3, 6, and 9 months, provided the bulk of our information to the Crystal Growth Branch of NRL. In this Final Technical Report, a synopsis is provided of that information already submitted on a variety of dates.

Measurements made at Western Washington University (WWU) under the terms of this project have been in accordance with a Statement of Work provided at the outset of the project. These include dc low-field electrical transport measurements in semi-insulating (SI) samples, as a function of temperature; observations of time dependent photoconductivity in this SI GaAs; and two types of optical transmittance measurement: in the near-infrared (near-IR) primarily for observation of absorption by EL2 defects, and in the mid-IR for observation of carbon local vibrational mode (LVM) absorption. Examples are provided in this Report of the four above-mentioned types of measurement. The WWU measurements have complemented work at NRL itself, of crystal growth under varied conditions, of low-temperature high resolution mid-IR and far-IR measurements, and of defect structure microscopic studies.

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INTRODUCTION

A program for growth from the melt of GaAs and other compound semiconductors by the VZM method was begun at NRL in the 1980s. A demonstration of the feasibility of this method for VZM growth of 'undoped' SI GaAs (in a pBN crucible) was reported by Swiggard [1] in 1989, and also by Henry *et al.* [2]. This writer (JSB) has had an opportunity to work with NRL on characterization aspects of the SI VZM crystals [3-9], where some of the published papers just cited involved work at WWU funded through a predecessor NRL project [Project N-00014-90-P-2030, for the period March 1990 to August 1991], while the most recent publications involve our work during the present 12-month contract [N-00014-92-P-2000]. Any interested reader of this report is invited to study the above-cited published papers for additional information about VZM-grown SI GaAs crystals and their properties.

As part of the introductory remarks, it is pertinent to note that the VZM GaAs crystals grown in the NRL program are of small size, compared with most melt-grown commercially produced GaAs crystals: a diameter of  $\sim 30$  mm, and an ingot weight of  $\sim 400$  g. This should be contrasted with the 75-100 mm diameter and overall 5-10 kg weight of commercial LEC crystals. Of course, use of a modest crystal size is sensible in R&D studies of an emerging technology, efficient in terms of energy use, and of the amount of expensive GaAs used. This does mean that a small VZM crystal has a larger surface-to-volume ratio, and accordingly that stoichiometry and surface chemical reactions influence some properties of this 'small' crystal more than would be the case for a 'scaled-up' crystal. One bulk GaAs property which we observe often to suffer as a result is the electronic mobility. Occasionally, a 300 K mobility of  $6,000 \text{ cm}^2/\text{V s}$  or more is measured, but many samples have mobilities in the  $4,000 - 5,000 \text{ cm}^2/\text{V s}$  range. Those in the GaAs IC industry who think in terms of LEC wafers for direct-implant MESFETs might be (momentarily) horrified, but they should not be. For the "highest and best" uses for wafers of VZM-grown SI GaAs can be expected to be as highly resistive substrates for epitaxial growth, and 'resistivity' is far more significant than 'mobility' for an epi-substrate.

Especially significant is the low dislocation density available by VZM growth of SI GaAs, which makes this material attractive as an epi-substrate for chips which include both electronic devices (HBTs, HEMTs, etc.) and optoelectronic components (lasers, LEDs, and detectors). Our goal during this project has been, and remains, reporting to the NRL Crystal Growth group about the electronic and optical properties of this high-resistivity low-EPD monocrystalline material. It has thus been possible for our results to influence the planning of the next round of crystal growth. The next several sections of this Final Technical Report deal with various aspects of measurements made at WWU during the 12-month period now ending.

NEAR-IR MEASUREMENTS (FOR EL2)

These are made at room temperature, by transmittance of a polished slab sample; corrected for multiple reflections, and converted (by computer, from point-by-point data, 1,000 points over the range  $1.0 - 1.5 \mu\text{m}$ ) into a graphical plot of absorption coefficient  $\alpha$  (in  $\text{cm}^{-1}$ ) versus wavelength or photon energy. Figure 1, on page 3, shows a typical example of one of the many VZM samples we have measured. The scalings reported by Martin (1981) for absorption by neutral EL2, and by Silverberg *et al.* (1988) for ionized EL2, are then used [3] to determine how much EL2 is present. This determination uses the number obtained from a nearby

[Text continues on page 4]

SAMPLE : VZM27-31N-II-1

DATE : 12/04/91

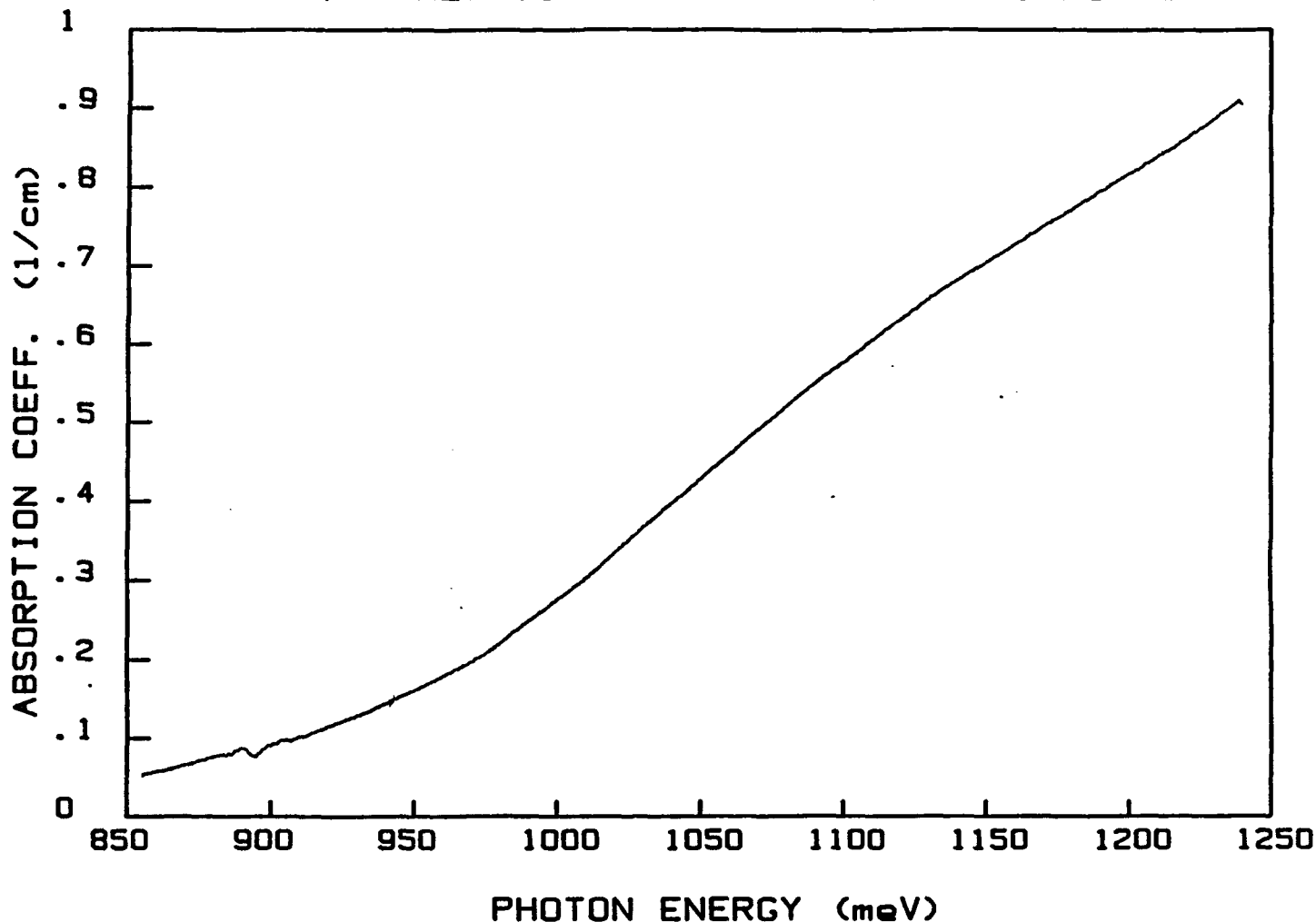


Figure 1: Near-IR absorption spectrum taken at 300 K for a polished slab sample ( $t = 3.44$  mm), deduced from transmittance data, with reflectance correction.

The shape is consistent with (mostly neutral) EL2 absorption. Electrical data for a nearby sample showed that  $P_1 = (N_{EL2}^+ / N_{EL2}) = 0.086$ . Thus the overall absorption shown here corresponds to  $N_{EL2} = (N_{EL2}^0 + N_{EL2}^+) = 8.1 \times 10^{15} \text{ cm}^{-3}$ .

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electrical sample, for the fraction  $P_i = (N_{EL2}^+ / N_{EL2})$  of those midgap defects which have become ionized by losing an electron. In the case of Sample VZM27-31N-II-1 illustrated by Figure 1, electrical measurements indicated that 8.6% of the EL2 were ionized at 300 K. The near-IR absorption then allows us to infer that  $N_{EL2} = 8.1 \times 10^{15} \text{ cm}^{-3}$  for this portion of Crystal 27-31N, of which 8.6% (i.e.,  $N_{EL2}^+ = 7.0 \times 10^{14} \text{ cm}^{-3}$ ) had been ionized by compensation.

These numbers are quite typical of the VZM-grown SI GaAs we have measured during the FY92 project year, for various ingots grown in an argon atmosphere. It appears to be possible to promote a larger total presence of EL2 in the upper part of a VZM crystal grown in a dense arsenic atmosphere [6], and of course SI GaAs commercially grown by the LEC method and then ingot annealed around 900°C usually does have a larger total EL2 concentration ( $\sim 1.6 \times 10^{16} \text{ cm}^{-3}$ ). This larger EL2 presence is desirable for SI GaAs wafers destined to be used in the manufacture of direct-implant MESFETs, since a larger EL2 concentration makes implant activation more efficient. However, having  $N_{EL2} \times 10^{16} \text{ cm}^{-3}$  is not important for the most likely application of VZM-grown material, as an epitaxial substrate for optoelectronics. For that application, the range  $6 - 9 \times 10^{15} \text{ cm}^{-3}$  for  $N_{EL2}$  which typically we find with VZM samples is quite adequate.

Apropos LEC-grown SI GaAs, for which an anneal  $\sim 900^\circ\text{C}$  is almost essential (to help relieve stress, in addition to defect chemical reactions which enlarge and homogenize EL2 content), it is interesting to note here that one recent VZM crystal was given a 6-hour 900°C anneal. (Crystal 28-15N, for which our measurements were in a Technical Report to NRL dated 09-10-92.) The anneal had no effect on the total EL2 concentration, and  $N_{EL2} = 7.75 \times 10^{15} \text{ cm}^{-3}$  was quite typical of the number found in other crystals which were continuously cooled from  $\sim 1200^\circ\text{C}$  to  $< 500^\circ\text{C}$ .

The last line of the first paragraph on this page indicates the ionized EL2 concentration ( $N_{EL2}^+ = 7.0 \times 10^{14} \text{ cm}^{-3}$ ) for material near the seed end of VZM crystal 27-31N. The actual number one finds for  $N_{EL2}^+$  depends, of course, on how compensation has occurred between shallow acceptors (notably  $C_{As}$ , but possibly also including  $Zn_{Ga}$  and/or  $Cd_{Ga}$ , depending on the source of the starting material), and shallow donors such as  $Si_{Ga}$ . Whereas the vertical zone process results in a carbon presence which decreases as one goes higher up a crystal (further from the seed cone), since  $C_{As}$  has a distribution coefficient greater than unity [10]; most other trace impurities have a distribution coefficient less than unity, and are swept by the molten zone towards the top (tail end) of an ingot. It has thus always been important for our measurements to report on samples from two, or even three, vertically-separated regions.

The above-discussed situation of  $N_{EL2}^+ \approx 7 \times 10^{14} \text{ cm}^{-3}$ , to make  $P_i$  lie within the range 0.07 - 0.10, is probably as near to ideal as one would wish for. One then has enough of the EL2 ionized so that control of the material's properties by EL2 is assured, without overdoing it. When  $P_i$  gets very large, say 0.25, then the material is quite close to intrinsic, and the resistivity is well up into the  $10^8$  ohm-cm range at 300 K. But with  $0.07 < P_i < 0.10$ , one has an electron concentration about ten times intrinsic, and a 300 K resistivity in the mid- $10^7$  ohm-cm range. This may sound higher than is fashionable nowadays for direct-implant MESFETs, but is great for an inert epi substrate.

## Near-IR Measurements for Cu-Diffused GaAs

As an adjunct to the observation by near-IR absorption in numerous samples of VZM-grown SI GaAs, we did have the opportunity during the period of this project to measure near-IR transmittance for some samples whose SI status had been modified

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by heat treatment, while exposed to copper. The copper diffusions were made by Dr. W. J. Moore at NRL, who then made He-temperature far-IR spectral measurements which showed that the low temperature Fermi energy locks onto the  $C_{As}$  acceptor level, rather than the considerably deeper  $Cu_{Ga}$  acceptor. That observation suggests a destruction of EL2 by copper. Our near-IR measurements, as exemplified by Figure 2 on page 6, support that hypothesis, which has recently been published [9], and to which any interested reader is referred for further details of this study. Figure 2 shows (apart from a water vapor caused artifact at 900 meV), a monotonic rise of (free hole) absorption as one goes to the left (towards longer wavelength, smaller  $h\nu$ ). There is no sign of the well-known absorption band caused by  $EL2^+$ , centered on 0.95 eV, with a gross width of  $\sim 0.3$  eV, and this shows that (at least almost) all of the EL2 has vanished. One postulate [9] is that  $Cu_{Ga}$  and  $As_{Ga}$  (the latter from EL2) form a double acceptor-double donor neutral complex. In any event, measurements with Cu-diffused samples added an interesting new dimension to our measurement work.

MID-IR ABSORPTION FOR CARBON LVM MEASUREMENT

The use of optical transmittance data in the mid-IR ( $\lambda_o \approx 17.25 \mu m$ ,  $\bar{\nu} \approx 580 \text{ cm}^{-1}$ ) to detect LVM absorption by  $C_{As}$  acceptors in GaAs has been widely adopted since the pioneering work of Brozel et al. in 1978. This, despite continuing discrepancies about the numerical conversion factor to be used - at room temperature or at low temperature - from LVM band integrated strength to the desired quantity: the substitutional carbon concentration  $N_{Carb}$ . This writer has summarized elsewhere [11] some of the relevant published literature, and proposed numbers for conversion factors which are at least consistent between low temperature data (more reliable but time-consuming to get) and the simpler room temperature data.

During the 1990-91 period of the earlier NRL-sponsored work, we had made crude observations of room-temperature transmittance in the carbon band region, using a Fourier transform IR (FTIR) instrument of only  $2 \text{ cm}^{-1}$  resolution. This was better than nothing, but only just. Just as Project N-00014-92-P-2000 began, WWU took delivery of a much better FTIR instrument (Mattson 5021) which can provide a resolution to  $0.4 \text{ cm}^{-1}$ . After experimenting with this machine, our conclusion has been that operation at  $0.75 \text{ cm}^{-1}$  resolution works best for getting a spectrum in a reasonable amount of time from which  $N_{Carb}$  can be deduced. Higher resolution just degrades the S/N ratio, and makes a much longer measurement time mandatory. After all, we seek only the area of the carbon LVM band, not the fine structure [11]. And so we have standardized on use of 128 scans (each, with and without sample) at  $0.75 \text{ cm}^{-1}$ . Measurements in this manner have been made for more than 40 VZM samples during the year now ending. A comprehensive report was made to NRL on 02-18-92 concerning  $N_{Carb}$  deductions for 35 GaAs samples, covering a 30:1 range of carbon content. More samples from more recent crystals have been reported on in subsequent Technical Reports. Also, a published account [8] has recently appeared in the Journal of Applied Physics concerning these data, and the computer procedure developed (by Mr. Saban at WWU) for numerical integration of the part of the absorption spectrum attributable to carbon LVM.

Figure 3 on page 7 shows one of the many examples from this year's work of a carbon LVM measurement. The example is not entirely typical, since this sample has much more carbon than most. We believe our limit of detection for  $N_{Carb}$  is  $\sim 1.5 \times 10^{14} \text{ cm}^{-3}$ . One could, of course, do better than this using 4.2 K data.

[Text continues on page 8]

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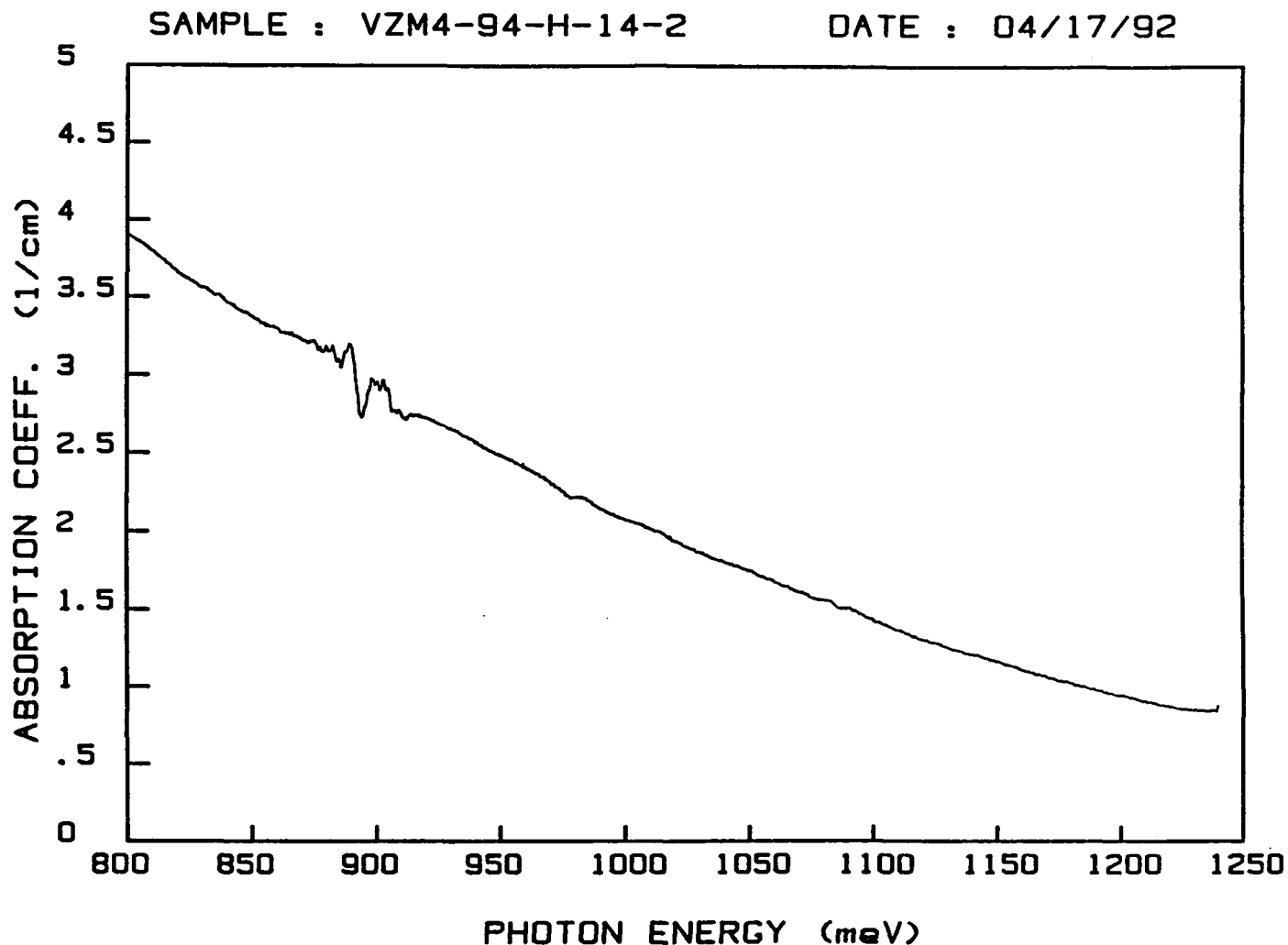


Figure 2: Near-IR absorption spectrum, derived from transmittance data obtained with a rather thin sample ( $t = 0.63$  mm) of material which originally had been semi-insulating [ $N_{EL2} = 7.3 \times 10^{15} \text{ cm}^{-3}$ , with  $N_{EL2}^+ = P_1 N_{EL2} = 6 \times 10^{14} \text{ cm}^{-3}$  in the as-grown state.] Copper diffusion for four hours at  $750^\circ\text{C}$  has converted the material to p-type. It also appears to have destroyed the EL2 originally present, since the spectrum above shows no sign of the  $EL2^+$  absorption band in the range  $0.95 \pm 0.15$  eV, only a featureless free hole absorption. (Ignore the artifact at 900 meV, caused by  $H_2O$  vapor.)

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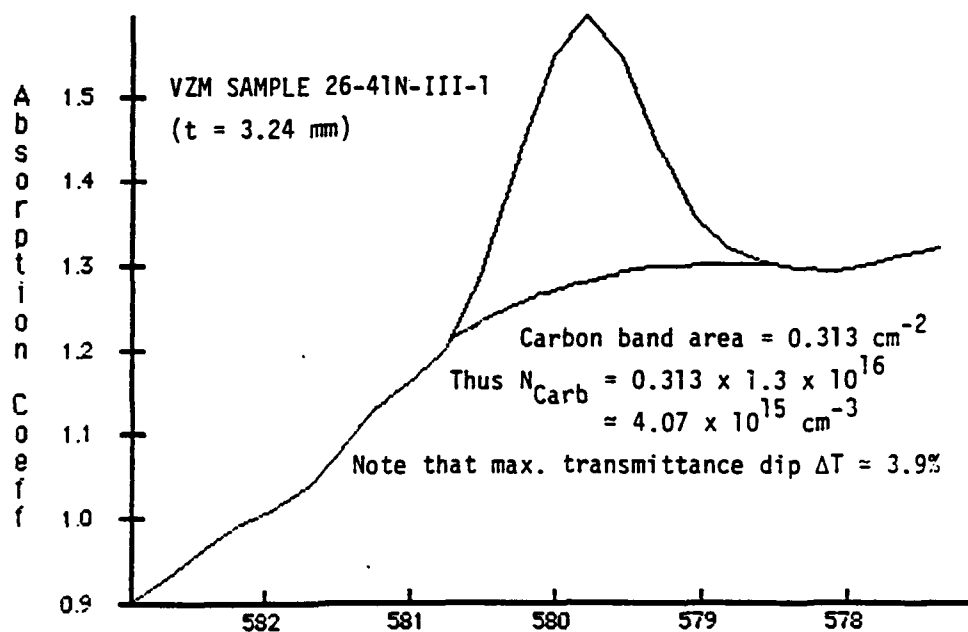
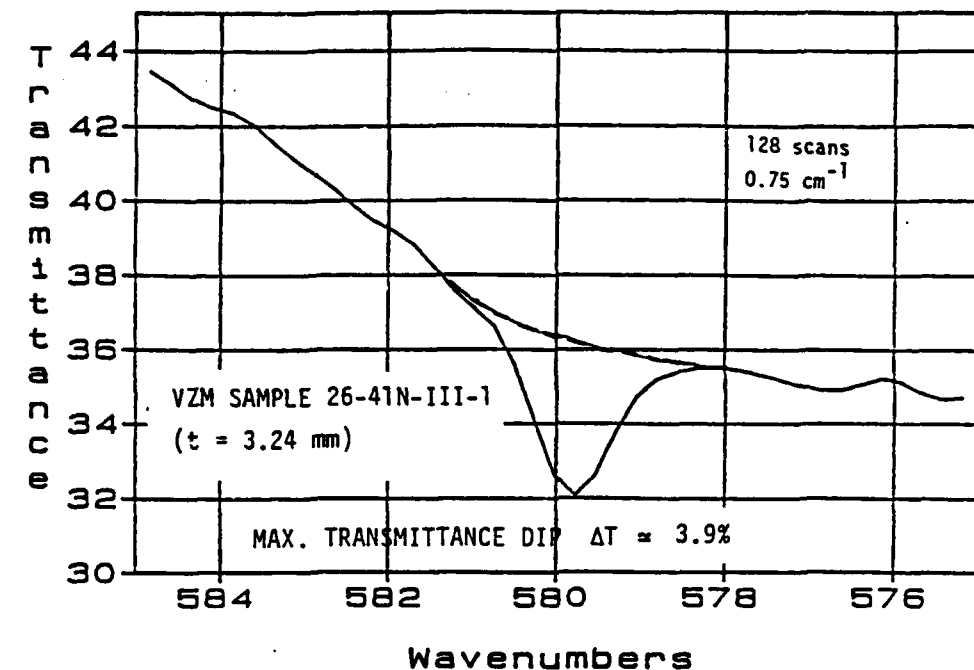


Figure 3: Data for one sample concerning carbon LVM absorption. At the top, the "raw" FTIR transmittance data. (This sample has more carbon than typical, so the "dip" shows prominently.) Below that, the same data converted into absorption coefficient, with the result of making a numerical integration of the area above a lattice absorption background curve.

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LOW-FIELD dc ELECTRICAL TRANSPORT MEASUREMENTS

For any semiconducting or semi-insulating crystalline solid, it is natural to want to know what the dc electrical properties are: at least for room temperature, and preferably for a range of temperature which gives some indications of (a) what controls the compensation, and (b) what controls the majority carrier mobility. Making such measurements with SI GaAs brings in some difficulties because of the high sample resistance, and many of the numbers quoted by commercial vendors for their SI GaAs are probably suspect! A serious effort was made by our group to be able to measure the dc transport properties with accuracy and reliability even up to the  $10^{10}$  ohm range which a SI GaAs sample can present slightly below 300 K, and has been applied to VZM material [4 - 6] in addition to GaAs from other sources [12]. Especially for near-intrinsic material, an ambipolar correction is necessary [13]; and the algebra involved in ambipolar correcting is useful, in any event, for deducing the fraction  $P_i$  of EL2 that has been ionized by compensation. Especially do we seek confirmation, from temperature-dependent transport measurements, that  $P_i$  changes only slightly with rising temperature - for this demonstrates that the Fermi energy is being controlled by the partial EL2 compensation.

Measurements of the kind just indicated have been made for VZM samples over the past several years, and have been continued during FY92 for samples from the various VZM crystals grown during the 12-month period of Project N-00014-92-P-2000. For illustration purposes in this report, data are used from Crystal VZM28-7N, which was measured during July 1992. Table I, on page 9, summarizes the 300 K electrical properties, reports (at the bottom of the table) on carbon LVM measurements, indicates the  $1.1 \mu\text{m}$  near-IR absorption caused by EL2, and uses this combination of EL2 absorption and (electrically deduced)  $P_i$  to work out the total EL2 presence. The table thus shows the rationale for the combination of measurements we make.

Table I shows that the ionized EL2 fraction in Crystal 28-7N decreased slightly from Section II ( $P_i = 0.084$ ) to Section III ( $P_i = 0.059$ ) higher up the crystal. Both of these numbers are highly satisfactory. For reasons discussed in the Introduction to this Report, "high" mobilities are not usually to be expected, and the two numbers shown in the columns of Table I are normal for a small-size crystal.

Table II, on page 10, shows the specific dc electrical transport data obtained at six temperatures from 296 K to 350 K. Note that mobility does decrease monotonically with rising temperature: a good sign indicative of the ordinary processes of optical phonon scattering, with none of the anomalous  $\mu_{\text{Hn}}(T)$  behavior one sees in a sample in which the EL2 compensation has microscopic spatial fluctuations. Another favorable sign in this data set is that  $P_i$  decreases quite slowly with rising temperature. This shows at a glance that any plot of  $\log(n_0)$  versus  $1/T$  would display the activation energy for EL2.

Prior to making transport measurements such as these examples, it is our practice to verify that the four contacts (at the corners of a square sample, for van der Pauw type measurement) are ohmic. The electric field is kept  $< 2 \text{ V/cm}$ , so that this is truly a "low-field" measurement. Thus, especially when  $T < 300 \text{ K}$ , the sample current needs to be a fully controlled one in the range of perhaps 50 pA to 500 pA.

[Text continues on page 11]



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Table I. An example of how our room temperature results are typically summarized for the set of samples from a given VZM-grown crystal. In this example, the crystal is VZM28-7N, for which measurements of the electrical and optical properties were measured during July 1992.

Crystal	VZM28-7N	
Optical Sample Slab	II-2	III-1
Electrical Data Wafer	II-5	III-4
<u>300.0K Electrical Data:-</u>		
Resistivity $\rho$ (ohm cm)	$5.63 \times 10^7$	$3.69 \times 10^7$
Hall Coeff. $R_H$ ( $\text{cm}^3/\text{Coulomb}$ )	$-2.60 \times 10^{11}$	$-1.77 \times 10^{11}$
Ratio $z = (R_{Hi}/R_H)$	11.1	16.3
Ambipolar-corrected Electron Hall Mobility $\mu_{Hn}$ ( $\text{cm}^2/\text{V s}$ )	4611	4795
Ambipolar-corrected Electron Concentration $n_o$ ( $\text{cm}^{-3}$ )	$2.84 \times 10^7$	$4.17 \times 10^7$
Ratio $(n_o/n_i)$	12.3	18.1
EL2 Ionized Fraction $P_i$	0.084	0.059
EL2 Concentrations (Neutral, Ionized, Total) Deduced from the above $P_i$ values, combined with room temp ( $\sim 295$ K) near-IR absorption data:		
1.1 $\mu\text{m}$ Absorption Coeff. $[\alpha (\text{cm}^{-1})]$	0.618	0.656
Deduced Neutral $N^o$ ( $\text{cm}^{-3}$ )	$7.02 \times 10^{15}$	$7.53 \times 10^{15}$
" Ionized $N^+$ ( $\text{cm}^{-3}$ )	$6.4 \times 10^{14}$	$4.7 \times 10^{14}$
Thus, Total EL2 Concentration $N_{\text{EL2}} = (N^o + N^+) (\text{cm}^{-3})$	$7.66 \times 10^{15}$	$8.00 \times 10^{15}$
Carbon, from room temperature LVM absorption measurements:		
Carbon band area ( $\text{cm}^{-2}$ )	0.158	0.079
$C_{\text{Carb}}$ deduced from the above, using $f_{\text{RT}} = 1.3 \times 10^{16} \text{ cm}^{-1}$	$2.05 \times 10^{15}$	$1.05 \times 10^{15}$

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Table II. A summary of data obtained at six temperatures for Sample VZM28-7N-II-5 ( $t = 0.45$  mm) of the low-field dc electrical transport properties. The table goes on to make an ambipolar conduction correction - which is numerically very small for this sample - and thereby evaluates the EL2 ionized fraction  $P_1$ .

DATE : 07/23/92

SAMPLE NAME : VZM28-7N-II-5

THICKNESS = 450 (MICRONS)

MAGNETIC FIELD = 5000 (GAUSS)

(VAN DER PAUW CORRECTION FACTOR  $f > 0.998$ )

TEMP. (K)	RESISTIVITY (OHM-CM)	HALL COEFFICIENT (CM <sup>3</sup> /COUL.)	HALL MOBILITY (CM <sup>2</sup> /VS)	CARRIER CONCENTRATION (CM <sup>-3</sup> )	1000/T (1/K)	Z
295.6	8.804E+7	-4.099E+11	4657	1.801E+7	3.382	11.34
300	5.630E+7	-2.595E+11	4611	2.836E+7	3.333	11.14
313.2	1.600E+7	-7.004E+10	4379	1.041E+8	3.192	10.73
325.9	5.120E+6	-2.139E+10	4179	3.380E+8	3.068	10.6
337.8	1.911E+6	-7.650E+9	4005	9.372E+8	2.96	10.42
349.9	7.478E+5	-2.856E+9	3821	2.489E+9	2.857	10.34

AMBIPOLAR CORRECTION DATA (CORRECTION FACTORS VERY CLOSE TO UNITY)

T (K)	Ei (mev)	Phi (mev)	Ni (cm <sup>-3</sup> )	No (cm <sup>-3</sup> )	Nd* (cm <sup>-3</sup> )	Ed (mev)	Ef (mev)	Pi 1/(1+No/Nd*)
295.6	712.2	40.3	1.438E+6	1.801E+7	1.658E+6	44	104.7	.0843
300	711.2	40.9	2.303E+6	2.836E+7	2.608E+6	44.1	105.8	.0842
313.2	708.2	42.7	8.753E+6	1.041E+8	9.420E+6	44.7	109.6	.083
325.9	705.3	44.5	2.865E+7	3.380E+8	2.944E+7	45.2	113.8	.0801
337.8	702.6	46.1	8.051E+7	9.372E+8	7.941E+7	45.7	117.5	.0781
349.9	699.8	47.7	2.147E+8	2.489E+9	2.036E+8	46.1	121.6	.0756

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TRANSIENT PHOTOCONDUCTIVE OBSERVATIONS IN VZM SI GaAs

As a trap-controlled crystalline solid, "undoped" SI GaAs has been known for more than 30 years to show a variety of responses to light. Even without any illumination, it is of course possible to create bizarre space-charge-limited current phenomena, using high electric fields and various kinds of injecting or non-injecting contacts. For the purposes of studying time-dependent photo-conductance, one would prefer to minimize contact phenomena, in order to observe the photo-generation of electrons and holes in the GaAs itself, and the capture of those photocarriers from the conduction and valence bands. While recognizing that this complex subject is unlikely to offer easy answers, we have felt that the potential promise of transient p.c. as a tool for characterization of SI GaAs makes it worthwhile trying. Some initial experiments have been made during the period of Project N-00014-92-P-2000, and more are contemplated in the future. Thus the account here shows just a few of the initial (and often strange) things detected - but not explained, so far!

Some of the background of this subject was analyzed in a 57-page "Technical Evaluation" prepared by the present writer, and submitted to NRL on 5-13-92. Among other things in that Evaluation was a contrast between the effects of sub-bandgap light ( $h\nu < 1.4$  eV,  $\lambda_0 > 900$  nm, for room temperature), and of above-bandgap illumination with more energetic photons. For sub-bandgap light has a penetration depth of several mm or more, and any photo-carrier creation which results will occur throughout the thickness of a sample. In contrast, above-bandgap photons have a penetration depth of  $1\ \mu\text{m}$  or less, and thus any p.c. effects one sees will arise from a very thin surface layer. With a bright source - such as a semiconductor laser - of above-bandgap light, one can create an electron-hole plasma strong enough to form essentially a short-circuit of a SI sample! Yet in contrast, generation of electrons and/or holes with sub-bandgap light (this generation occurring primarily at EL2 sites, since they outnumber all other kinds of point defects) is likely to be quite inefficient. Based on what has been reported for the capture coefficients of  $\text{EL2}^+$  (for electron capture) and of  $\text{EL2}^\circ$  (for hole capture), one should expect an electron lifetime  $\tau_n \sim 50$  ns, and a hole lifetime  $\tau_p$  perhaps as much as 100 times larger. Despite this, the relatively larger efficiency of electron release by  $\text{EL2}^\circ$  photoionization, and the larger mobility of electrons compared with holes, means that electron-related p.c. will often be stronger than hole-related p.c. Much depends on the wavelength of the sub-bandgap light used, and on the time domain studied.

Our observations to date have used two light sources, which can be used either separately or in combination: (a) For above-bandgap light - penetrating only within the first  $1\ \mu\text{m}$  of depth - an AlGaAs laser diode with a 780 nm output wavelength; maximum of 15 mW optical output, which one can operate either continuously or pulsed, for which we use a Melles Griot laser driver. Pulses down to  $< 20$  ns duration can be provided, with any desired duty cycle. (b) For penetrating sub-bandgap light, we have used a small grating monochromator with quartz-halogen-tungsten lamp, using a filter to block above-bandgap second order components. The output wavelength can be set in the interesting range  $0.9 - 1.6\ \mu\text{m}$  ( $0.78 - 1.4$  eV). This sub-bandgap light can be used dc, or chopped (equal on/off times) at a frequency of from  $\sim 1$  Hz to 1 kHz.

Figure 4 (page 12) shows a circuit we used in our preliminary p.c. experiments, for conversion of a transient signal into compatibility with a  $50\ \Omega$  measurement system. Transients have been collected by a Tektronix 2430A digital 'scope, which nominally has a 2.3 ns response time, though we are unlikely to challenge that limit.

[Text continues on page 13]

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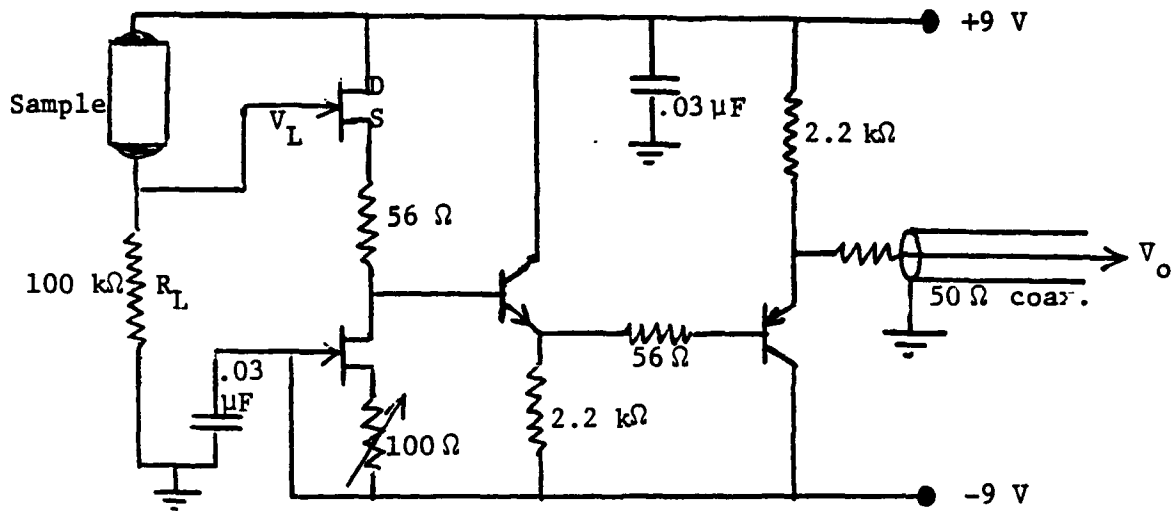


Figure 4: Circuit used in the preliminary p.c. experiments, for impedance transformation from the high sample resistance to the 50 Ω oscilloscope input.

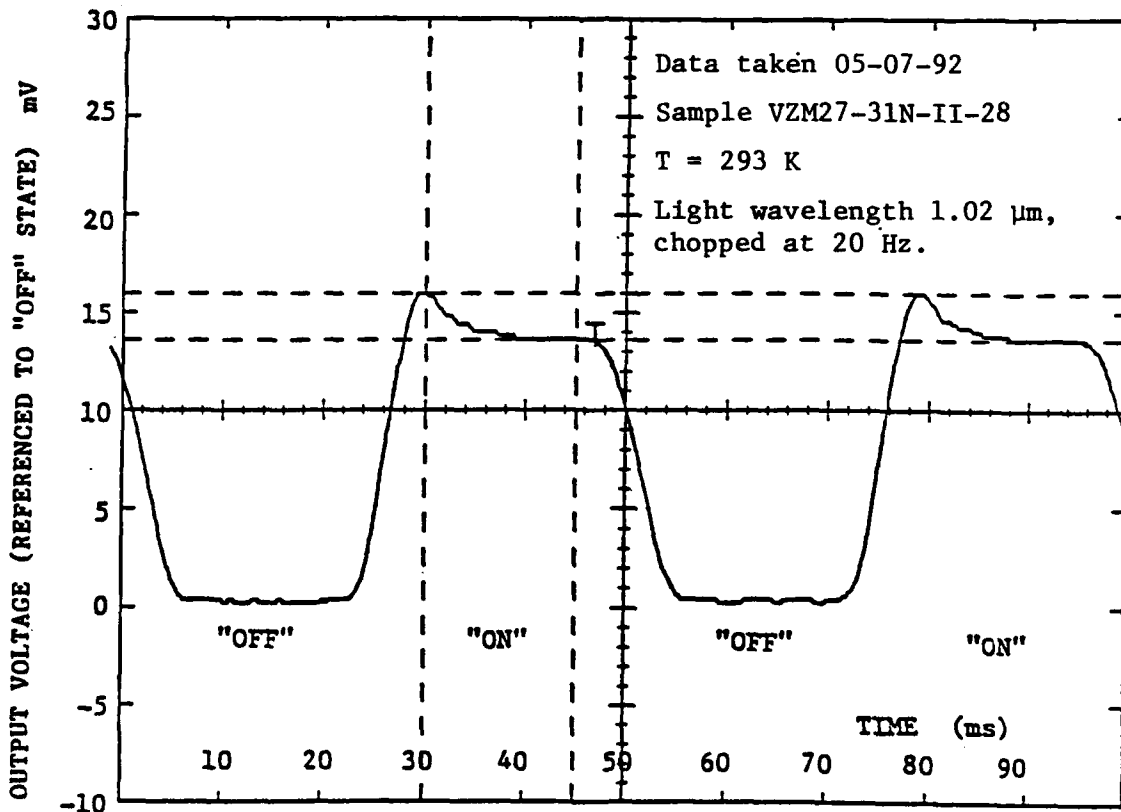


Figure 5: A typical example of the p.c. response (in the circuit of Fig. 4) to sub-bandgap light, slowly chopped. The oscilloscope uses 50 Ω input, dc coupled, and the trace is the result of averaging  $\sim 100$  transients. Note the overshoot as the "ON" part of the cycle begins.

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Indeed, although we have seen some interesting multiple-time-constant transients in the time regime from  $\sim 500$  ns to  $100 \mu\text{s}$ , there have also been some much slower transient events to surprise us.

Since SI GaAs has a 300 K resistivity in the dark of  $>10^7 \Omega \text{ cm}$ , the corresponding dielectric relaxation time  $\tau_D = (\kappa \epsilon \rho) > 10 \mu\text{s}$ , more than 100 times slower than the expected electron capture time  $\tau_D$  at ionized EL2. There can thus be no hope of observing any fast capture processes by transient p.c. unless the dielectric relaxation time is made much smaller, either by heating (not the most attractive solution) or by using "background" d.c. illumination. Thus the sub-bandgap penetrating light mentioned on page 11 was initially thought of simply as a way to make  $\tau_D$  smaller, allowing observation of rather fast transients from laser pulses. This is still part of the game plan, but it turned out that remarkable very slow transients occur just with the "background" light turned on/off with a chopper. Figure 5 (on page 11) shows a typical example: we have seen analogous "overshoots" with this and other SI samples. One can vary what happens by changing the illumination conditions, even producing an initial overshoot, followed by a "droop", and then a slower rise again. The light intensity (photon flux) can be varied to see different aspects, and so can the illuminating wavelength. (Note that light of  $\sim 1.0 \mu\text{m}$  wavelength is absorbed most efficiently, and almost entirely in EL2<sup>0</sup> photoionization to create excess electrons. Light of  $\sim 1.3 \mu\text{m}$  wavelength is much less efficient at creating photoelectrons, but is optimized for creation of photoholes by photoneutralization of EL2<sup>+</sup>.) It also appears possible that what one sees as the chopper sweeps "ON" may depend on how long it has previously been "OFF". To test this in any future experiments, it would be desirable to be able to adapt our chopper wheel for an ON/OFF duty cycle different from 1:1.

Figures 6 and 7, on page 14, exemplify the variety of transient patterns one can observe using chopped  $1.3 \mu\text{m}$  light, this sample #5 (VZM27-12N-II-5) having a 295 K dark resistivity of  $\sim 7 \times 10^7 \Omega \text{ cm}$ , and  $\mu_{Hn} \approx 5800 \text{ cm}^2/\text{V s}$ . Figure 6 shows a prominent overshoot at the beginning of the 'ON' period, and the largest amplitude one of these [curve (d)] corresponds to the middle trace in Figure 7. From Fig. 7, one finds - just as with other SI samples, that a slow rise during the 'ON' period becomes dominant when the chopping frequency is further reduced.

This feature is even more prominent when  $1.0 \mu\text{m}$  light is used, as exemplified by Figures 8 and 9 on page 15. There is a range of intensity for which the initial overshoot is the most prominent feature; while for higher photon flux, the slow rise is dominant. When one uses very slow chopping and high intensity, our data (not illustrated) show the signal taking  $>100$  ms just to reach 50% of its "final" value.

Lest any reader wonder whether these strange slow transient phenomena are caused by the measuring circuit, we believe this can be discarded since there is nothing "strange" about the signal as it reaches the baseline of "light off". It is not thermal (bolometric) either, despite the large temperature dependence of dark resistivity for SI GaAs; for we have experimented with and without good heat sinking of the sample - and get the same results. It is possible that the data of Figures 5 - 9 is connected with the emission time coefficients of the two charge states EL2<sup>0</sup> and EL2<sup>+</sup>, and this merits further investigation.

Using the sub-bandgap light as a dc "background" illumination, we have also measured the response characteristics of SI samples to pulses of 780 nm (i.e., above bandgap) light. Figure 10 on page 16 shows that the amplitude of the p.c. response to laser pulses does depend on whether background light is present, and its quality. At least this aspect went as expected. However, the rise-time and fall-time characteristics of the response were not simple exponentials, and have to be described

[Text continues on page 17]

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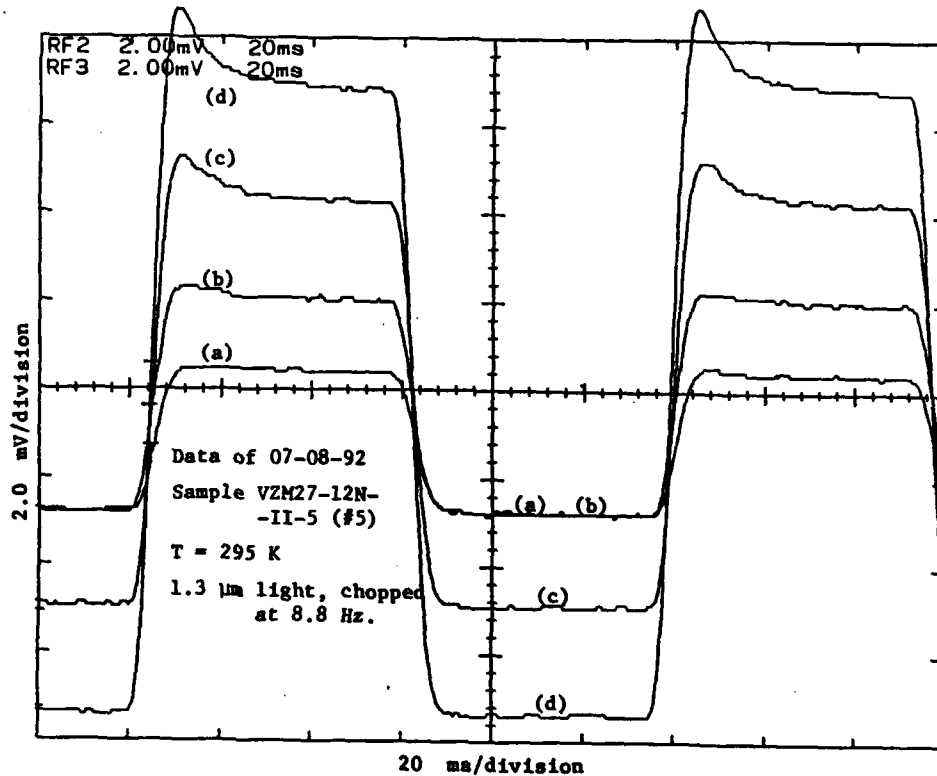


Figure 6: Response of Sample #5 (VZM27-12N-II-5) to slowly chopped 1.3  $\mu$ m light, at four intensities to increase the post-overshoot 'plateau' response height from (a) 3.2 mV to (d) 14.5 mV.

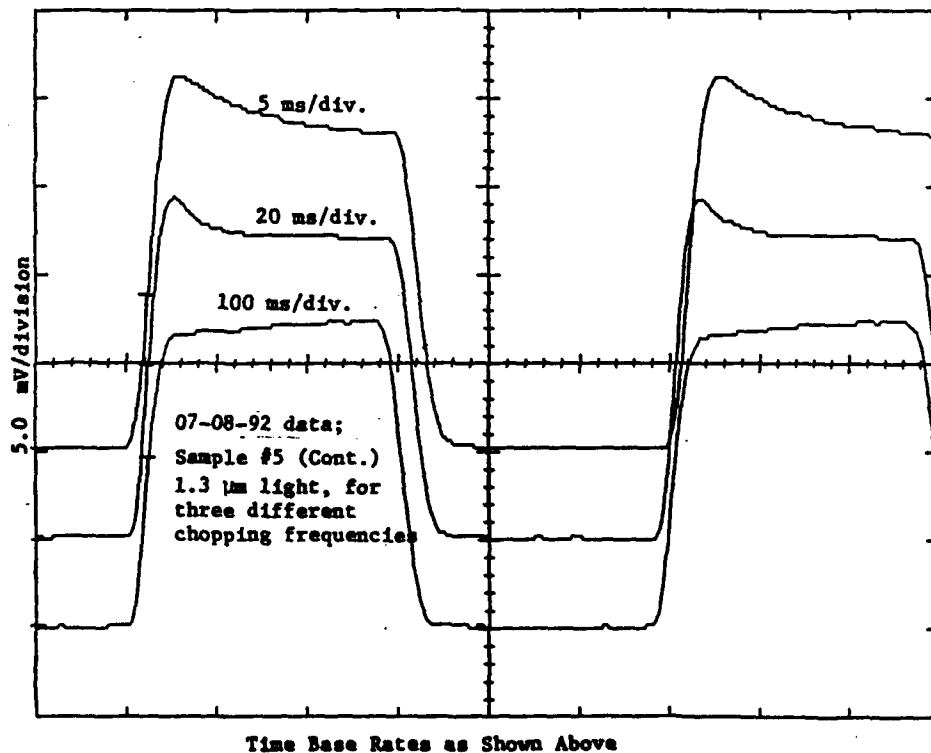


Figure 7: Still 1.3  $\mu$ m light, same intensity as in (d) above, but shown for three chopping speeds. With long 'ON' and 'OFF' times, a different time-dependence can be seen.

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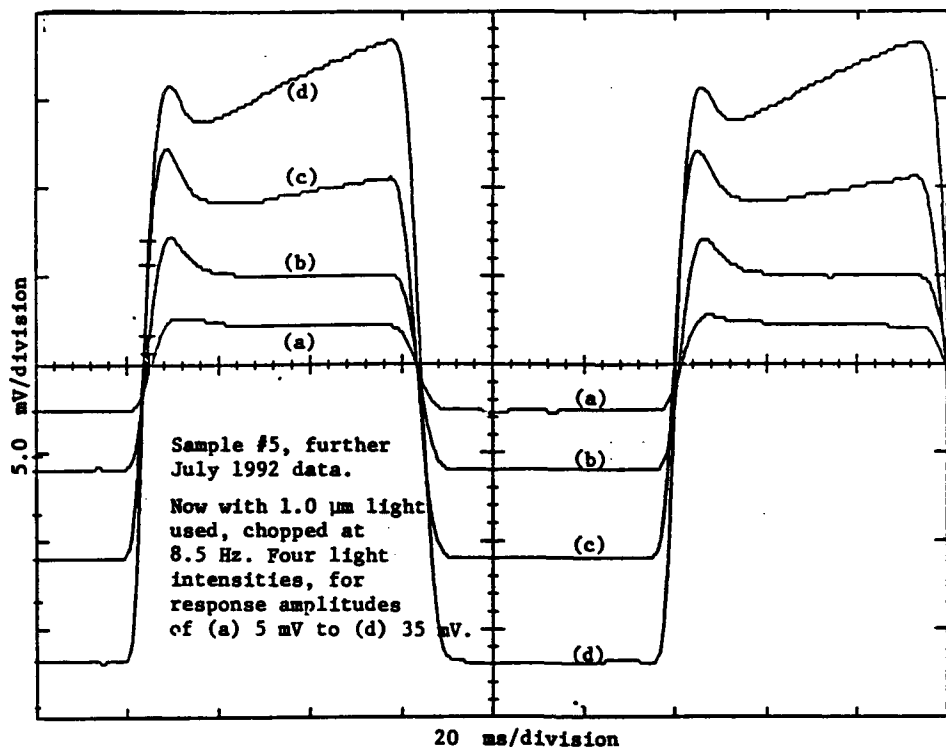


Figure 8: More data for Sample #5, with slowly chopped sub-bandgap light, now of 1.0  $\mu\text{m}$  wavelength (four intensities). Note that for the two higher intensities, the initial overshoot is followed by a slower climb.

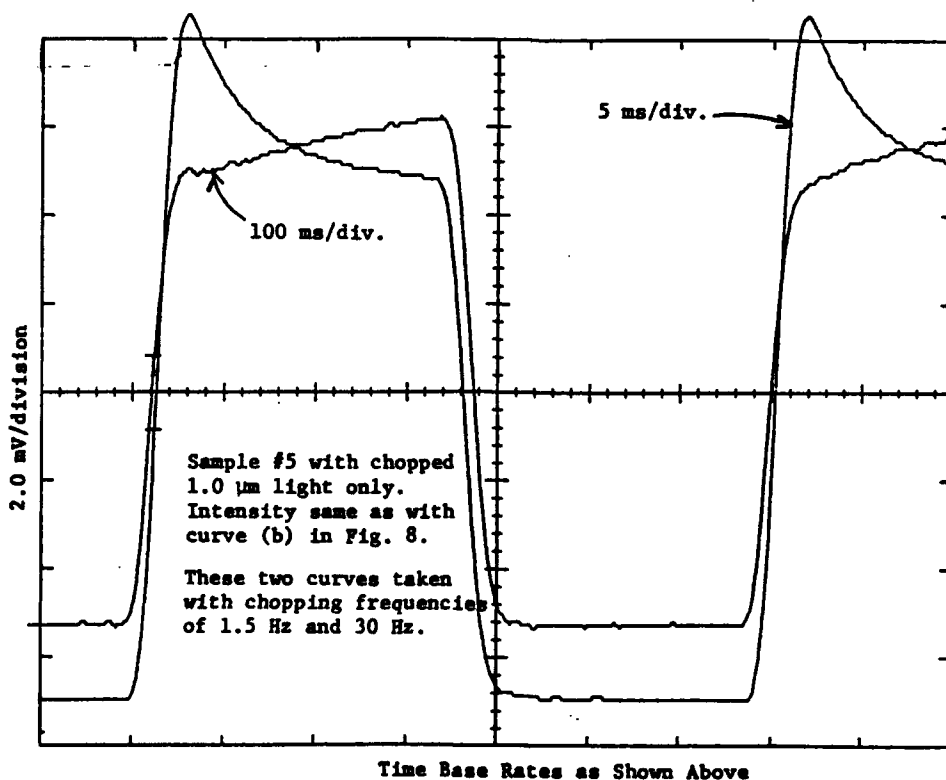


Figure 9: The temporal sequence further demonstrated for 1.0  $\mu\text{m}$  chopped light by using a faster or a slower chopping rate. This suggests that the length of the "OFF" time is significant.

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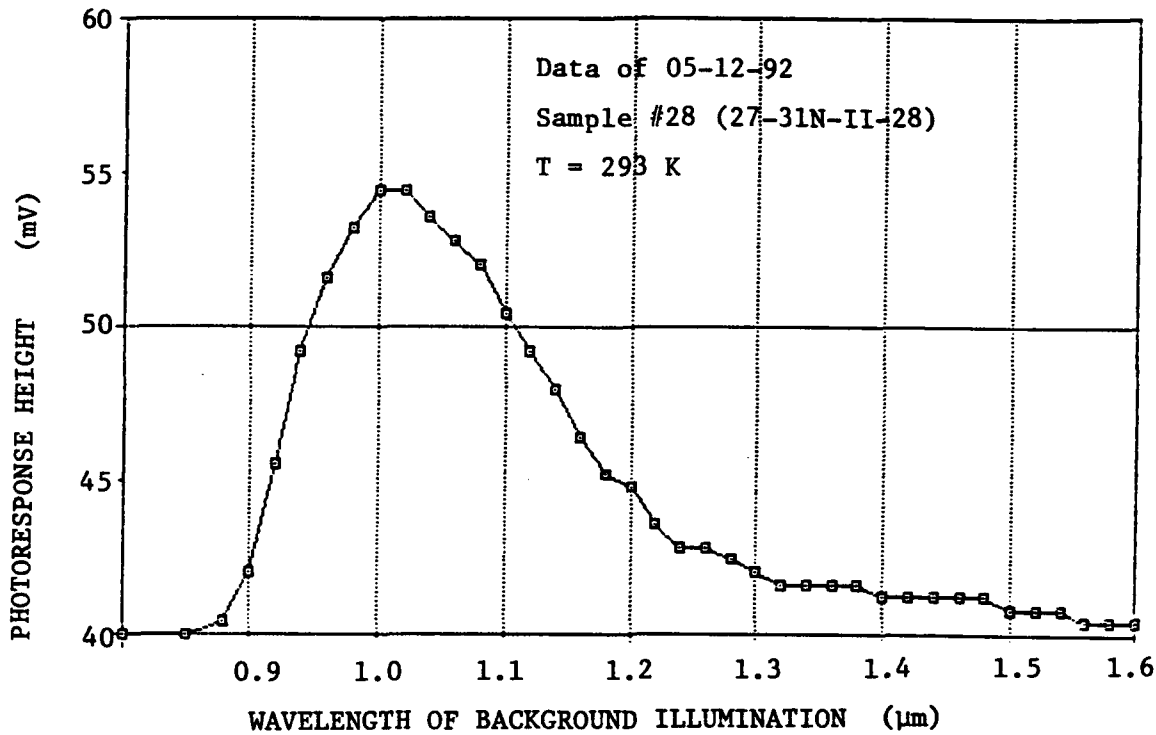


Figure 10: Response of a sample to laser pulses ( $\lambda_o = 780 \text{ nm}$ , duration  $200 \mu\text{s}$ ), showing the p.c. response height versus the wavelength used for background light.

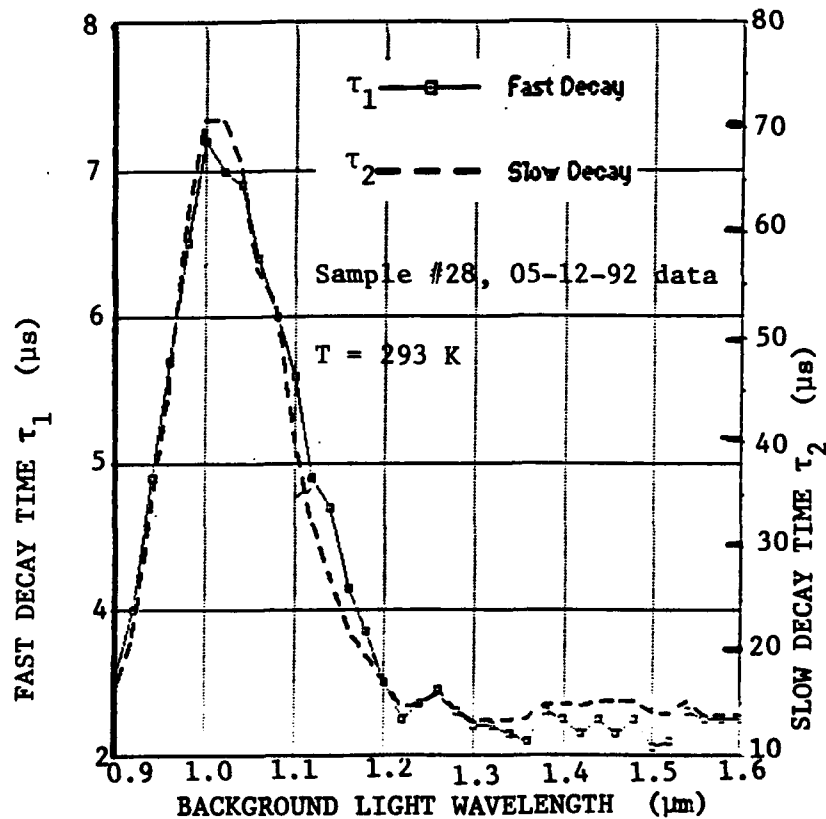


Figure 11: One example of how the fast and slow components of decay after a laser pulse are affected by the wavelength chosen for background light.



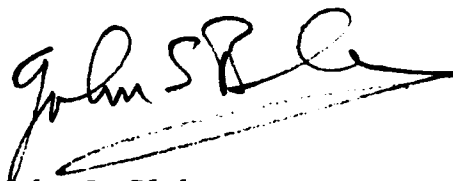
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at the least by "fast" and "slow" components. Figure 11 on page 16 shows one example of the time constants for fast decay ( $\tau_1$ ) and slow decay ( $\tau_2$ ) as these were affected by the wavelength chosen for background light. In other experiments, with Sample #28 and others, we have observed - depending on laser intensity, and background light wavelength and intensity - components of rise and decay with time constants of less than 1  $\mu$ s, and slow "tails" extending over hundreds of  $\mu$ s.

Despite these confusing complexities, it is the opinion of this writer that further experimentation with transient p.c. of SI GaAs (such as VZM-grown GaAs) may eventually allow an additional dimension to the assessment of melt-grown crystals. If any defect entities other than EL2 are present, and affect the transient p.c. response, it would be valuable to be able to detect them, with all the analytic methods available.

With the above comments on a "characterization" method which is still far from established - but which shows an interesting range of phenomena - I bring this Report to a conclusion. The NRL-grown VZM crystals for which the vast majority of our measurements are made, continues to show promise as a substrate material for epi-based optoelectronic integration, by virtue of its low EPD. Our electrical and optical measurements are able to keep a check on how changes in the growth process affect the resulting monocrystals, and provide a feedback loop to the Crystal Growth Section of NRL. The results of both the crystal growth and characterization activities are also made available to the semiconductor community at large by open publication - see Appendix A on page 18, Items 1 - 9.

Respectfully submitted,

A handwritten signature in dark ink, appearing to read "John S. Blakemore", with a long horizontal flourish extending to the right.

Dr. John S. Blakemore  
Principal Investigator

Appendices: Page 18, Appendix A, Citations

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APPENDIX A: CITATIONS

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- [2] R. L. Henry, P. E. R. Nordquist, R. J. Gorman, and S. B. Quadri, J. Crystal Growth 109, 228 (1991).
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